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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention adds a polymer raw material in more detail about a composite material to a swelling laminar silicate, the ionic compound which has an alkoxycarbonyl group, the composite material containing a catalyst, and this composite material, and relates to melting and/or the composite-ized polymeric material produced by polymerizing.

[0002]

[Description of the Prior Art]In order to improve the various characteristics of polymer, such as polyester and polyamide, especially a mechanical property, and heat resistance conventionally, mixing and kneading inorganic materials, such as calcium carbonate, argillite, and mica, has been performed. However, only by mixing and kneading these inorganic materials, since an inorganic material cannot serve as microscopic particles easily and does not distribute, what has the characteristic which should be satisfied is not obtained.

[0003]Therefore, the chemical treatment of montmorillonite or the fluoride mica system expansive clay mineral is carried out, atomization is tried, and much patent application is made about the invention which aimed at the uniform dispersion to the inside of an organic molecule. As those examples, JP,62-74957,A, JP,2-173160,A, JP,3-7729,A, JP,3-41149,A, JP,8-3310,A, JP,8-59822,A, JP,8-120071,A, and JP,8-134205,A are mentioned. However, even if it copes with it by these techniques, the actual condition is the dispersibility which should be satisfied enough in practice not having been acquired, but remarkably influenced by the difference in the composite-ized polymer kind.

[0004]A dispersing agent is added to montmorillonite or a fluoride mica system expansive clay mineral, atomization is tried, and patent application is made also about the invention which aimed at the uniform dispersion to the inside of an organic molecule. As those examples,

JP,10-168182,A which used polyphosphate salt and polynuclear metal complex salt as a dispersing agent, and JP,11-80586,A using potassium pyrophosphate as a dispersing agent are mentioned.

[0005]The polyester composite material (PET) which used as the raw material the organicity-ized silicate which added bromination tetrabutylphosphonium to the slurry of synthetic fluoride mica is indicated by JP,11-1605,A. However, compared with PET in which this PET does not contain a laminar silicate, about 10 to 20% of the mechanical strength is improving.

[0006]

[Problem(s) to be Solved by the Invention]This invention aims to let the composite-ized polymeric material which was excellent in a mechanical strength or heat resistance melting and/or by polymerizing in the polymer raw material provide the composite material obtained.

[0007]

[Means for Solving the Problem]A swelling [this invention persons] laminar silicate, an ionic compound which has a COOR basis (R is an alkyl group), and a composite material containing a catalyst, It finds out that a composite-ized polymeric material which added to a polymer raw material and was excellent in a mechanical strength and heat resistance melting and/or only by polymerizing is obtained, and came to complete this invention.

[0008]That is, this invention includes the following inventions.

(1) A swelling laminar silicate, an ionic compound which has a COOR basis (R is an alkyl group), and a composite material containing a catalyst.

(2) A composite material given in the above (1) acquired by making a swelling laminar silicate, an ionic compound which has a COOR basis (R is an alkyl group), and a catalyst dissolved or suspended to a solvent.

[0009](3) A composite material the above (1) whose ionic compound which has said COOR basis is any one sort of a phthalic acid derivative which has a COOR basis, a naphthalene-dicarboxylic-acid derivative which has a COOR basis, and the phosphonium salt derivative which has a COOR basis, or two sorts or more, or given in (2).

(4) A composite material given in either of aforementioned (1) - (3) in which said swelling laminar silicates are swelling synthetic mica.

(5) The above (1) A polymer raw material is added to a composite material given in either of - (4), and they are melting and/or a composite-ized polymeric material produced by polymerizing.

(6) A composite-ized polymeric material given in the above (5) in which said polymer raw material is a polyester raw material.

[0010]

[Embodiment of the Invention]As described above, this invention adds a polymer raw material to a swelling laminar silicate, the ionic compound which has a COOR basis (R is an alkyl

group), the composite material containing a catalyst, and this composite material, and relates to melting and/or the composite-ized polymeric material produced by polymerizing.

[0011]The details of ** polymer raw material which constitutes the composite-ized polymeric material of an ionic compound ** catalyst and this invention which has a ** swelling laminar silicate ** COOR basis (R is an alkyl group) which constitutes the composite material of this invention are shown below.

[0012]** With the swelling nature of a swelling laminar silicate swelling laminar silicate. It is a meaning in which water or an organic solvent advances and swells between crystal layers in water or an organic solvent, and a difference is produced in a degree of swelling according to the kind of the element which constitutes a main composition layer, and element which constitutes the substance between layers, it becomes what is called free swelling or limited swelling, and each can be used in this invention. Those swelling laminar silicates serve as micro crystallite of a thin film integrated circuit underwater, and are distributed.

[0013]The crystal structure of the swelling laminar silicate used by this invention consists of a substance between layers which consists of a main composition layer (2:1 layers) with which the tetrahedron sheet (A) and the octahedron sheet (B) were combined at a rate of A:B=2:1, and a positive ion which is among those layers in order to maintain electric charge balance. It is better to grind the swelling laminar silicate used by this invention, when a thing with a mean particle diameter of 0.1-50 micrometers is preferred and particle diameter is large.

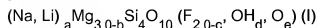
[0014]As an example of the swelling laminar silicate used by this invention, For example, nature or composite hectorite, saponite, a SUCHIBUN site, Smectite group argillite, such as beidellite, montmorillonite, nontronite, and bentonite, Swelling mica group argillite, such as Na-type tetra silicic fluoride mica, Li type tetra silicic fluoride mica, a Na salt type fluoride TENIO light, and Li type fluoride TENIO light, and vermiculites, these substitution products and derivatives, or these mixtures are mentioned. That by which some of Na ion of the ion between layers or Li ion are replaced with K ion, and the thing by which some Si ion of the tetrahedron sheet is replaced with Mg ion are contained in said substitution product.

[0015]As a commercial item, RAPONAITO XLG (Britain, rapport company composition hectorite allied substances), RAPONAITO RD (Britain, synthetic hectorite allied substances by a rapport company), Sir MABISU (a German country, the Henkel KGaA composition hectorite allied substances), smecton SA-1 (the Kunimine Industries saponite allied substances), Bengel (the natural montmorillonite of **** Traveling-abroad sale, and KUNIPIAF (natural montmorillonite of the Kunimine Industries sale).) Veegum (natural hectorite by the U.S. and Vanderbilt), a DAIMO night (synthetic swelling mica by Topy Industries, Ltd.), SOMASHIFU (ME-100, synthetic swelling mica by CO-OP CHEMICAL CO., LTD.), SWN (synthetic smectite by CO-OP CHEMICAL CO., LTD.), SWF (synthetic smectite by CO-OP CHEMICAL CO., LTD.), etc. are mentioned.

[0016]The swelling synthetic mica produced by heat-treating the mixture of talc and cay fluoridation alkali in said swelling laminar silicate is preferred, What is produced by heat-treating the impalpable powder which mixed talc, sodium silicofluoride, and/or cay lithium fluoride at 600 ° - 1200 ° is still more preferred. Specifically, the swelling synthetic mica shown by formula (I) is mentioned.

[0017]

[Formula 1]



[0018]The positive ion of the coordination number 12 which has $(\text{Na}, \text{Li})_a$ between layers among [type, The positive ion of the coordination number 6 in which $\text{Mg}_{3.0-b}$ forms the octahedron sheet, and Si are the positive ions of the coordination number 4 which forms the tetrahedron sheet, and F of $(\text{F}_{2.0-c}, \text{OH}_d, \text{O}_e)$, OH, and O exist in an octahedron sheet as negative ion. in addition -- " -- " -- and/or, "is expressed. The sign of a-e expresses the following numerical value.

$0.2 \leq a \leq 1.0; 0 \leq b \leq 0.5; c = d + 2e \leq 1.0; 0 \leq d \leq 1.0; 0 \leq e \leq 0.5$ [0019]** As an ionic compound which has a COOR basis used by ionic compound this invention which has a COOR basis (R is an alkyl group), In molecular structure, it has a basis of the ionicity of carboxylate ion, sulfonate ion, etc. with a COOR basis (R is an alkyl group), for example, It will not be limited especially if it is a polymer raw material (it indicates to ** for details), melting, and/or a compound that may polymerize, Although R (alkyl group) of the COOR basis of an ionic compound may be an alkyl group which has a substituent, It is preferred that it is the straight chain or branched alkyl group expressed with $\text{C}_n \text{H}_{2n+1}$ - (n is an integer), What is especially an alkyl group of the carbon numbers 1-30 is preferred, what is an alkyl group of the carbon numbers 1-4 is still more preferred, and what is CH_3 - and C_2H_5 - is the most preferred.

[0020]As such an ionic compound, a cationic compound which has a COOR basis, and an anionic compound which has a COOR basis are mentioned. A cationic compound which has a COOR basis is a compound which can carry out an ionic bond to a stratification plane of a swelling laminar silicate, and a phosphonium salt derivative etc. which have a COOR basis are mentioned as such an ionic compound.

[0021]As a phosphonium salt derivative which has a COOR basis, To a phosphorus atom, an aryl group which is not replaced [substitution or] (for example, phenyl group), A substituent chosen from an aralkyl group (for example, benzyl), an alkyl group of the carbon numbers 1-20, and a divalent hydrocarbon group of the carbon numbers 1-20 (a substituent of these) At least one sort of chemical structure chosen from hydroxyl, a carboxyl group, a carbonyl group, an epoxy group, vinyl bonds, an ester bond, and an ether bond may be included. It is the

united thing, What a basis which has a COOR (R shows alkyl group) basis combined with at least one basis is mentioned, What a basis which has especially COOR (R shows an alkyl group of the carbon numbers 1-4) combined is preferred, and what a COOCH₃ group and a COOC₂H₅ group combined is still more preferred.

[0022]Specifically, EOTP (3-carboethoxy-2-oxo propyl triphenyl phosphonium chloride), MTP (carbomethoxy methyltriphenylphosphonium star's picture), etc. are mentioned. An anionic compound which has a COOR basis is a compound which can carry out an ionic bond via a stratification plane and a catalyst (it indicates to ** for details) of a swelling laminar silicate, and carboxylate and a sulfonate which have a COOR basis are mentioned as such an ionic compound, for example.

[0023]As carboxylate which has said COOR basis, For example, a monoester derivative of aromatic dicarboxylic acid, such as phthalic acid (phthalic acid, isophthalic acid, terephthalic acid) and naphthalene dicarboxylic acid. (For example, TMP (terephthalic acid monomethyl potassium)); as for mono- ** of aromatic tricarboxylic acid, such as benzene tricarboxylic acid and naphthalene tricarboxylic acid, diester derivative; etc. are mentioned.

[0024]As a sulfonate which has said COOR basis, For example, a benzenesulfonic acid salt which has a COOR basis; A sulfonate by which, as for mono- ** of said aromatic dicarboxylic acid, a sulfonic group was introduced into a diester derivative. (For example) [STPDM and (2-sulfodimethyl terephthalate sodium)] SIPDM (5-sulfoisophtharate dimethylsodium), monosulfo-2,6-naphthalene-dicarboxylic-acid dimethylsodium; sulfonate; etc. into which a sulfonic group was introduced are mentioned to mono- ** JI or a triester derivative of said aromatic tricarboxylic acid.

[0025]** Add a catalyst catalyst in order to enable it to perform efficiently melting with a polymer raw material, and/or a polymerization. A catalyst used by this invention will not be limited especially if melting of a composite material and a polymer raw material and/or a polymerization are promoted. A catalyst used by this invention is a catalyst for polymers manufacture, and a transesterification catalyst which is used, for example in the case of polyester besides a polymerization catalyst etc., a catalyst used when carrying out melting to a polymer raw material, etc. are mentioned.

[0026]Specifically, a metal system catalyst using metal salt is mentioned. transition metal of metal is preferred -- especially -- the [periodic table] -- a transition metal belonging to IV - a group VIII is preferred. A catalyst used by this invention has especially a preferred thing distributed to an organic solvent among these. Specifically an alkoxide of a germanium salt, an antimony salt, zinc salt, and titanium, etc. are mentioned, especially an antimony salt is preferred, and SbCl₃ is still more preferred.

[0027]** The composite-sized polymeric material of polymer raw material this invention can add

a polymer raw material to a composite material of this invention, and can obtain it melting and/or by polymerizing to it. In this invention, a polymer raw material means a raw material for polymers manufacture. As such a polymer raw material, especially if a composite-ized polymeric material can be formed, it will not be limited, but specifically, a monomer, oligomer, low polymerization degree polymer, polymer, etc. are mentioned. In a composite-ized polymeric material of this invention, one sort of a polymer raw material or two sorts or more are used.

[0028]In this invention, it is preferred to use a raw material of thermoplastics as a polymer raw material, and specifically, Polymer raw materials, such as polyester, polyamide, polyester amide, polyether, polyether ester, polyurethane, acrylic resin, phenol system resin, and polyolefines (polyethylene, polypropylene, polystyrene, etc.), are mentioned.

[0029]A monomer of polyamide which is typical polymer, and polyester is indicated below. As an example of a polyamide monomer, 6-amino-n-caproic acid, Lactam, such as nylon salt, such as adipate of amino acid, such as 12-amino dodecanoic acid, and hexamethylenediamine, epsilon caprolactam, a butyrolactam, a valerolactam, capryl, and dodecanolactam, etc. are mentioned.

[0030]As a polyester monomer being concrete, as dicarboxylic acid or its diester, Adipic acid, suberic acid, azelaic acid, sebacic acid, DOTEKAN diacid, Terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, 2-chloroterephthalic acid, 5-methyliso phthalic acid, 5-sodium sulfoisophtharate, hexahydro terephthalic acid, Hexahydro isophthalic acid, diphenyldicarboxylic acid, diphenyl ether dicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, diglycolic acid, dimethyl terephthalate, screw hydroxyethyl terephthalate (BHET), etc.; Again as diol (glycol), Ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanediol, neopentyl glycol, a diethylene glycol, 1, 4-bis(beta **HIDOROKISHI ethoxy) benzene, a polyethylene glycol, a polypropylene glycol, polytetramethylene glycol, etc. are mentioned.

[0031]As oligomer or low polymerization degree polymer, polyamide, polyester, A low molecular weight body of polymer, such as polyester amide, polyether, polyether ester, polyurethane, acrylic resin, phenol system resin, and polyolefine, is mentioned, and it consists of at least one of sorts of these. Also in this, polyamide, oligomer of polyester, and low polymerization degree polymer are used general-purpose.

[0032]In the case of polyester, specifically Aromatic polyester, aliphatic polyester, It is oligomer of unsaturated polyester, low polymerization degree polymer, and alkyd resin, and the esterification reaction of dicarboxylic acid and diol which are polyester monomers is carried out under application of pressure, or a polycondensation is carried out under decompression of oligomer like BHET, and it is manufactured. What carried out low molecule quantification of the polyester by hydrolysis, a pyrolysis, etc. is used.

[0033]As for a solid thing, it is preferred among these polymer raw materials to grind and use it. Although a process of a composite material of this invention is described below, this invention is not limited to this. A composite material of this invention contains an ionic compound and a catalyst which have a swelling laminar silicate and a COOR basis.

[0034]A composite material of this invention is obtained by making a catalyst an ionic compound which has a swelling laminar silicate given in **, and a COOR basis given in ** preferably, and given in ** dissolved or suspended to water or an organic solvent. An organic solvent dissolves an ionic compound which has a COOR basis, and a polyhydric alcohol class containing alcohols and glycols (lower alcohol, such as methanol, ethanol, and propanol etc.) is mentioned.

[0035]Water or an organic solvent was made to distribute suspension of a swelling laminar silicate, and an addition is usually 0.1 to 1 % of the weight preferably 0.01 to 10% of the weight. As for an ionic compound which has a COOR basis, what was dissolved in a solvent is preferred, and although the addition changes with kinds, it is 1 - 70meq preferably 0.1 to 100 meq to a swelling laminar silicate, and is 1 - 30meq still more preferably.

[0036]When a catalyst is dissolved in a solution made to dissolve this compound in an organic solvent, and also an ionic compound which has a COOR basis adds a swelling laminar silicate in the case of a compound which has a cation at the time of distribution and is mixed to it, a composite material of this invention is obtained. When organic solvent liquid in which a catalyst was dissolved, and dispersion liquid which made water distribute a swelling laminar silicate are mixed in the case of a compound which has an anion at the time of distribution, and a compound which has a COOR basis adds this compound into this mixed liquor and is mixed into it, a composite material of this invention is obtained.

[0037]Although an addition of a catalyst changes with metaled kinds, it is 5 to 20 % of the weight still more preferably one to 30% of the weight preferably 0.5 to 50% of the weight to a swelling laminar silicate. A composite-ized polymeric material of this invention adds a polymer raw material given in ** to an obtained composite material, and is obtained melting and/or by polymerizing.

[0038]An addition of a swelling laminar silicate to a polymer raw material is 0.2 to 5 % of the weight preferably 0.1 to 20% of the weight. Thus, a composite-ized polymeric material of this invention obtained is excellent in a mechanical strength and heat resistance.

[0039]

[Example][Composition of example 1 composite-material A] EOTP of 30meq considerable amount was added and dissolved in 100 ml of ethanol solution to swelling synthetic mica (CO-OP CHEMICAL [CO., LTD.] make: ME). Having added 1 ml of solutions adjusted by SbCl_3 2 g/IPA100ml, and stirring this solution, 2.5 g of slurries were added slowly 8% of the weight which made water distribute ME, and also it stirred for 30 minutes, and suspension was

obtained. This suspension was dried and the composite material A of this invention was obtained.

[0040][Composition of example 2 composite-material B] The composite material B of this invention was obtained like Example 2 except having set EOTP of 30meq considerable amount of Example 1 to MTP of 12meq considerable amount.

[Composition of example 3 composite-material C] 2.5 g of 8-% of the weight slurries of ME were put into 50 ml of water, it stirred for 30 minutes, and ME suspension was obtained. Next, in 50 ml of IPA solutions in which SbCl_3 0.03g was dissolved, SIPDM of 12meq considerable amount was added to ME suspension and ME, and also it stirred for 30 minutes in them, and suspension was obtained in them. This suspension was dried and the suspension of the composite material C of this invention was obtained.

[0041][Composition of example 4 composite-material D] The suspension of the composite material D of this invention was obtained like Example 1 except having made ME of Example 1 into natural montmorillonite (KUNIPIAF of the Kunimine Industries sale).

[0042][example 5 Composition [of a composite-ized polymeric material (PET)]] Under the environment which added a 0.2g considerable amount to BHET10g by ME conversion of composite material A-D of this invention manufactured in Examples 1-4, and performed the nitrogen purge to it, After making it dissolve at 275 **, carried out the full vacuum, and hold for 4 hours, it was made to polymerize at this temperature, and composite-ized polymeric material (PET) A-D of this invention was compounded.

[0043][Composition of comparative example 1 comparison PET A (blank)] In the raw material, BHET was polymerized by the publicly known method (the BHET method), and the comparison PET A (blank) was compounded. [Composition of comparative example 2 comparison PET B (ME content)] After adding the amount part of ME duplexs to BHET100 weight section and mixing for 3 minutes, it polymerized by the publicly known method (the BHET method), and the comparison PET B (ME content) was compounded.

[0044][Measurement of example of experiment 1 mechanical strength (bending strength)] Composite-ized polymeric material (PET) A-C compounded by Example 5 and the comparative example and the comparison PETA and B were processed into the following size, and the mechanical strength [bending strength: Δf_B (Kg/cm²)] was measured.

[0045] $\Delta f_B = 3PL_v/2Wh_2P$: Load (Kgf) when [at which the specimen broke] it breaks
L: distance 4cmWbetween length 5cmL_v:fulcrums: of a specimen -- width 0.5cmh_v: of a specimen -- the height 0.2-cm result of a specimen is shown in Table 1.

[0046]

[Table 1]

		曲げ強さ : $\delta f B$ (Kgf/cm ³)
実施例	複合化ポリマー材料 (PET) A	1.352
	複合化ポリマー材料 (PET) B	1.092
	複合化ポリマー材料 (PET) C	1.308
比較例	比較PET A (ブランク)	710
	比較PET B (ME含有)	810

[0047][Experimental result] The bending strength close to 1.5 to twice is obtained to the comparison PET A with a blank composite-ized polymeric material of this invention. One 1.3 to 1.7 times the outstanding flexural strength of this is obtained also to the comparison PET B which made ME contain by a publicly known method. (Refer to Table 1)

[0048]

[Effect of the Invention]The composite material of this invention has heat resistance. Since quality is stable, it is useful as a raw material of the industrial process which manufactures adhesives, a paint, various plastics, textiles, and these, and useful as a raw material of the composite-ized polymeric material excellent in especially a mechanical strength and heat resistance.

The composite material and polymer raw material of this invention are added, melting and/or the composite-ized polymeric material produced by polymerizing have a good moldability, and it is excellent in a mechanical strength and heat resistance.

[Translation done.]